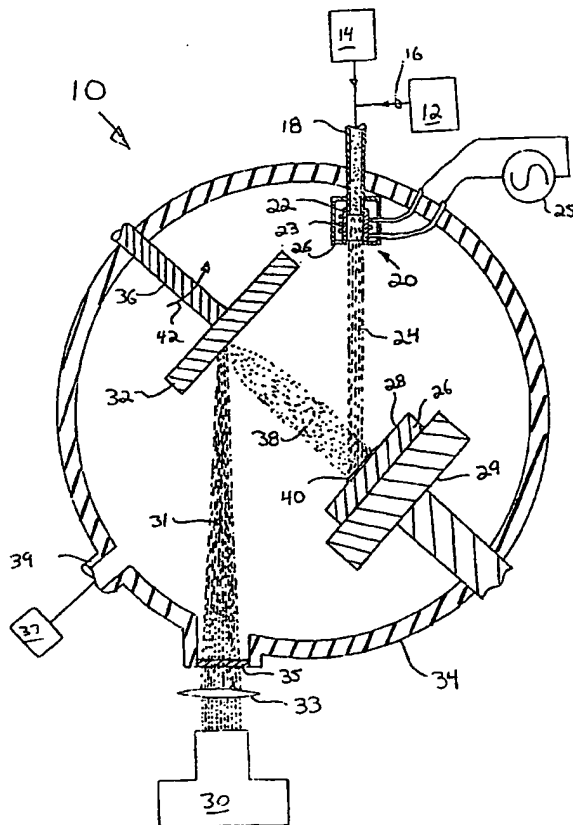




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<p>(21) International Application Number: <b>PCT/US94/07964</b> (22) International Filing Date: <b>15 July 1994 (15.07.94)</b> (30) Priority Data: 08/092,020      15 July 1993 (15.07.93)      US 08/145,967      29 October 1993 (29.10.93)      US (60) Parent Applications or Grants (63) Related by Continuation US      08/092,020 (CIP) Filed on      15 July 1993 (15.07.93) US      08/145,967 (CIP) Filed on      29 October 1993 (29.10.93) (71) Applicant (for all designated States except US): <b>PRESIDENT AND FELLOWS OF HARVARD COLLEGE [US/US]; 17 Quincy Street, Cambridge, MA 02138 (US).</b> (72) Inventors; and (75) Inventors/Applicants (for US only): <b>LIEBER, Charles, M. [US/US]; 27 Hayes Avenue, Lexington, MA 02173 (US). NIU, Chunming [CN/US]; 104 Conwell Avenue, Somerville, MA 02144 (US).</b></p>	<p>(74) Agents: <b>BROOK, David, E. et al.; Hamilton, Brook, Smith &amp; Reynolds, P.C., Two Militia Drive, Lexington, MA 02173 (US).</b> (81) Designated States: <b>AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).</b> <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i></p>	
<p>(54) Title: <b>EXTENDED NITRIDE MATERIAL COMPRISING <math>\beta</math>-C<sub>3</sub>N<sub>4</sub></b></p> <p>(57) Abstract</p> <p>An extended nitride material comprises <math>\beta</math>-C<sub>3</sub>N<sub>4</sub>. A method of forming an extended nitride material includes forming an atomic nitrogen source, forming an elemental reagent source and combining the atomic nitrogen and elemental reagent to form the extended nitride material. The elemental reagent is reactive with the atomic nitrogen of the atomic nitrogen source to form the extended nitride material. The apparatus of the invention can include, for example, a radio-frequency (rf) discharge nozzle for forming the atomic nitrogen source, such as an atomic nitrogen beam. The elemental reagent source can be formed by employing a pulsed laser to ablate a suitable target, such as a graphite target, to thereby form an ablation plume of elemental carbon. The ablation plume and the atomic nitrogen beam combine and cause the elemental carbon reagent and the atomic nitrogen to react and form the extended nitride material. The extended nitride material can accumulate as a film on a suitable substrate, such as Si(100) or polycrystalline nickel.</p>		



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EXTENDED NITRIDE MATERIAL COMPRISING  $\beta$ - $C_3N_4$ Background of the Invention

There is a great demand in industry for new materials. Of especial importance is development of materials which have extreme physical properties that can substitute for expensive known materials. Diamond, for example, is industrially useful because it is the hardest known material. However, even synthetically-formed diamond is very expensive.

At least one material has been identified which, hypothetically, would have a bulk modulus (and corresponding hardness) comparable to that of diamond. This material, like diamond, would be an extended solid, but would have an empirical formula of  $\beta$ - $C_3N_4$  and could be a superior alternative to many known materials, including diamond. However,  $\beta$ - $C_3N_4$  would be metastable, as are other similar nitride materials.

Examples of failed attempts to form  $\beta$ - $C_3N_4$  have included plasma decomposition of methane and nitrogen gas, and pyrolytic decomposition of C-N-H type organic compounds. Both methods have formed only C-N-H type solids and have not yielded any evidence of  $\beta$ - $C_3N_4$ . It has been suggested that the relative stability of hydrocarbon and N-H type reaction products under the conditions of the plasma decomposition and pyrolytic decomposition methods have precluded formation of  $\beta$ - $C_3N_4$ .

Another example of an attempt to form  $\beta$ - $C_3N_4$  has been shock wave compression of C-N-H type precursors. Although diamond has been formed by this method, there has been no evidence of  $\beta$ - $C_3N_4$ .

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Summary of the Invention

The present invention relates to an extended nitride material wherein at least a portion of the material has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ , and to a method and apparatus of forming an extended nitride material, such as  $\beta\text{-C}_3\text{N}_4$ .

The method includes forming an atomic nitrogen source and an elemental reagent source. The elemental reagent source includes an elemental reagent, such as carbon, boron, silicon or titanium, which is reactive with atomic nitrogen of the atomic nitrogen source to form the extended nitride material. The atomic nitrogen and the elemental reagent are combined to cause the atomic nitrogen and the elemental reagent to react and form the extended nitride material.

The apparatus includes means for forming an atomic nitrogen source and means for forming an elemental reagent source, whereby atomic nitrogen and the elemental reagent can react to form the extended nitride material.

Advantages of the present invention include, for example, the ability to form metastable nitride materials. Among the materials that can be formed are those, such as  $\beta\text{-C}_3\text{N}_4$ , which have not been successfully formed by conventional methods. Further, the materials formed can have superior physical properties and can be employed advantageously as substitutes for relatively expensive existing materials and for materials formed by known methods.

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#### Brief Description of the Drawings

Figure 1 is a plan view of one embodiment of the apparatus of the present invention.

Figures 2a-2c are a series of plots of Rutherford backscattering spectra recorded on 3  $\mu\text{m}$  thick C-N films formed by the method of the present invention using one, four, and twelve percent nitrogen gas in helium.

Figure 3 is an electron diffraction pattern recorded on material from a C-N film formed by the method of the present invention, wherein the film contained sixty percent carbon and forty percent nitrogen, and using an electron beam energy of about 120 keV.

Figure 4 is a Rutherford backscattering spectrum (RBS) acquired with a glancing angle geometry.

#### Detailed Description of the Invention

The features and other details of the method of the invention will now be more particularly described with reference to the accompanying drawings and pointed out in the claims. It will be understood that the particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principle features of this invention can be employed in various embodiments without departing from the scope of the invention.

The present invention includes a method and apparatus for forming an extended nitride material. One embodiment of the apparatus of the invention is shown in Figure 1. Apparatus 10 of Figure 1 includes means for forming an atomic nitrogen source and means for forming an elemental reagent source which is

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reactive with atomic nitrogen of the atomic nitrogen source to form the extended nitride material.

Preferably, means for forming an atomic nitrogen source include nitrogen gas source 12 and inert gas source 14. An example of a suitable inert gas is helium. Conduits 16 and 18 extend from nitrogen gas source 12 and inert gas source 14, respectively, and intersect for combination of nitrogen and a suitable inert gas in conduit 18. Conduit 18 extends to radio-frequency discharge source 20. In a particularly preferred embodiment, radio frequency discharge 20 source includes aluminum oxide ( $Al_2O_3$ ) nozzle 22 and coil 23. Coil 23 is connected to a suitable power source 25. Housing 26 extends about nozzle 22 and coil 23. An example of a suitable housing is a housing formed of copper (Cu). Radio frequency discharge source 20 is suitable for directing an atomic nitrogen source, such as atomic nitrogen beam 24 formed by exposure of nitrogen gas to radio-frequency discharge at radio-frequency discharge source 20, to substrate 26 at surface 28.

Substrate 26 is mounted on supporting heater 29. Examples of suitable substrates include Si(100), polycrystalline nickel, other suitable metals, etc. Suitable metal substrates can be at least one component of an article of manufacture, such as a cutting tool for material fabrication, or a bearing surface.

In one embodiment, means for forming the elemental reagent source include laser 30, which can form laser beam 31, and target 32. Examples of suitable lasers include Nd:YAG and excimer lasers. Lens 33 is positioned between laser 30 and window 35 of vessel 34. Lens 33 is suitable for focusing laser beam 31 onto

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target 32. Target 32 is formed of a suitable material for forming a plume of elemental reagent which, when combined with the atomic nitrogen of the atomic nitrogen source, will react with the atomic nitrogen to form the extended nitride material. Examples of suitable targets include carbon-nitride, graphite, silicon, boron and titanium targets. A preferred target is graphite. A particularly preferred target is oriented pyrolytical graphite. Target 32 is mounted on rotating support 36.

Target 32 and substrate 28 are sealed within vessel 34. Vacuum source 37 extends from opening 39 of vessel 34. Target 32 is positioned in vessel 34, relative to laser 30 and substrate 26, to cause an ablation plume of elemental reagent, formed by ablation of target 32 with laser beam 31, to extend to surface 28 of substrate 26. In one embodiment, target 32 is substantially parallel to, and about four centimeters from, surface 28 of substrate 26.

In one embodiment of the method of the invention, helium, which has been seeded with nitrogen gas, and which is at relatively high pressure, such as about 50 and 300 Torr, is directed through aluminum oxide nozzle 22. Atomic nitrogen beam 24 is formed by exposure of the nitrogen gas to radio frequency (rf) discharge within aluminum oxide nozzle 22 of radio frequency discharge source 20. In one embodiment, the radio frequency discharge supplied to nitrogen passing through aluminum oxide nozzle 22 is sufficient to produce a flux of atomic nitrogen which is greater than about  $10^{18}$  atoms  $\text{sr}^{-1}\text{s}^{-1}$  and having kinetic energies less than about five electron volts. The atomic nitrogen

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beam is directed to surface 28 of substrate 26. Preferably, vacuum source 37 is activated to maintain the absolute pressure with vessel 34 in the range of between about  $1 \times 10^{-7}$  and  $1 \times 10^{-5}$  Torr.

An elemental reagent source is formed, such as by ablation of target 32, which is rotating, as indicated by arrow 42, with laser 30 to form ablation plume 38 of the elemental reagent. In the embodiment wherein the target is graphite, ablation plume 38 includes atomic carbon and carbon chains of various chain lengths.

The atomic nitrogen of the atomic nitrogen source, and the elemental reagent, i.e. elemental carbon, of the elemental reagent source, combine at substrate 24 to react and form extended nitride material 40. When the elemental reagent employed is carbon, the nitride material is a carbon-nitrogen solid film. An "extended nitride material," as that term is employed herein, means a continuous, as opposed to particulate or granular, solid phase. In one embodiment, the extended nitride material includes only a single component, such as  $\beta\text{-C}_3\text{N}_4$ . Alternatively, the extended nitride material includes  $\beta\text{-C}_3\text{N}_4$  and various impurities, such as elemental or molecular impurities. An example of such an impurity is oxygen.

The relative amounts of the atomic nitrogen and elemental reagent which react to form the resulting nitride material can be controlled, for example, by controlling the rate at which the atomic nitrogen source is formed and the relative rate at which the elemental reagent source is formed. In a particularly preferred embodiment, the relative rates at which the atomic nitrogen source and elemental carbon of an



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elemental carbon source are formed causes at least a portion of the resulting extended nitride material, which is formed by reaction of the atomic nitrogen and elemental carbon reagent, to be  $\beta$ - $C_3N_4$ .

For example, in one embodiment, the nitrogen gas content in the helium which is subsequently exposed to radio frequency discharge has a concentration in the range of between about one and about twelve percent, by volume, of the combined nitrogen and helium gases. The radio frequency discharge is about one hundred fifty watts, the substrate is Si(100) and the laser employed is a frequency-doubled Quanta Ray GCR-16 laser, that provides eight nanosecond pulses of five hundred and thirty-two nanometer wavelength light with an energy of three hundred millijoules per pulse. A particularly preferred laser is an ultraviolet laser having a wavelength of about one hundred and ninety-three nanometers. Examples of other suitable lasers include: a frequency-tripled Nd-YAG laser emitted a wavelength of about 353 nanometers; a frequency- quadrupled laser emitting a wavelength of about 266 nanometers; a Kr-excimer laser emitting a wavelength of about 146 nanometers; an Xe-excimer laser emitting a wavelength of about 172 nanometers; an XeCl-excimer laser emitting a wavelength of about 318 nanometers; and an Ar-excimer laser emitting a wavelength of about 125 nanometers. The laser output can be shifted by a suitable nonlinear optical technique.

A ten millimeter diameter gaussian output from the laser is focused to a spot on a graphite target surface having a diameter of about two millimeter diameter and at a position off the rotation axis of the target.

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Preferably, the resulting atomic nitrogen beam and the ablation plume accumulate on the substrate, which is heated to a temperature in the range of between about 165 and 600°C by supporting heater 29, to form an extended nitride film having a thickness in the range of between about 0.1 and about five microns.

The invention will now be further and specifically described by the following examples. All parts and percentages are by weight unless otherwise stated.

#### Exemplification

##### Example 1

A pulsed Nd:YAG laser was used to ablate a high-purity graphite target within a stainless steel vacuum chamber. The ablation plume, which contained a variety of carbon fragments, was directed at a diametrically opposed substrate (Si(100) or polycrystalline Ni) located about 4 cm from the target.

An atomic nitrogen beam was formed by a radio frequency (rf) discharge within an Al<sub>2</sub>O<sub>3</sub> nozzle through which a relatively high pressure (≈100 torr) N<sub>2</sub>-seeded He gas flow passed. This source produced a very high flux of atomic nitrogen ( $\geq 10^{18}$  atomic sr<sup>-1</sup>s<sup>-1</sup>) with kinetic energies in the range of between about 0.1 and one electron volt.

The apparatus shown in Figure 1 was used to prepare a series of carbon nitrogen thin films where the relative flux of atomic nitrogen and substrate temperature were systematically varied during growth. Absolute pressure was maintained in the range of between about  $1 \times 10^{-5}$  and  $1 \times 10^{-4}$  torr during formation of the extended nitride material. In all cases the

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chemical composition of the films was determined with Rutherford backscattering spectroscopy (RBS). Representative RBS data obtained on a series of C-N films grown on Si(100) substrates with a 150 W rf discharge and 1, 4, and 12% N<sub>2</sub> in He are shown in Figure 2.

It was immediately evident upon examination of the RBS data that the fraction of nitrogen in the C-N films increased systematically as the percentage of atomic nitrogen in the atomic beam source was increased from about one to about twelve percent. Quantitative analysis of the RBS data showed that the use of beams with 1, 4, and 12% atomic nitrogen yielded C-N films with average nitrogen contents of 15, 28, and 41%, respectively.

In addition, several experiments were carried out to determine the influence of the source of nitrogen and substrate growth temperature. Importantly, essentially no nitrogen (<1%) was incorporated into films prepared by laser ablation of graphite with the rf-discharge off or in a background of 200 mtorr of N<sub>2</sub>; that is, these films consisted only of amorphous carbon. Hence, the generation and reaction of atomic nitrogen with the elemental carbon and carbon fragments produced by laser ablation was essential to the formation of the C-N films. Secondly, film growth between 165°C and 600°C had little effect on the C:N ratio in the films. These data indicated that within this temperature range, the reaction between laser generated carbon and atomic nitrogen dominated the formation of the C-N materials.

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Data addressing the chemical nature of these C-N materials was also obtained. X-ray photoelectron spectroscopy measurements (XPS) (Surface Science, Model 206) showed that the C-1s and N-1s binding energies in the C-N films were 284.6 and 399.1 eV, respectively. The observed C-1s binding energy was comparable to that observed (284.3) in diamond thin films. More importantly, the observed N-1s binding energy was comparable to that found in molecules with covalent C-N bonds. In contrast, the N-1s binding in boron nitride (a solid in which there was significant charge transfer from boron to nitrogen) was about 1 eV smaller than we observed. The XPS data thus indicated that carbon and nitrogen formed an unpolarized covalent bond in these new C-N materials, and thus our experimental results agreed with earlier theoretical suggestions that there was almost no charge transfer between C and N. The C-N films prepared with the atomic nitrogen source also exhibited excellent adhesion to both Si and Ni substrates, and furthermore, scratch tests indicated that these films were qualitatively hard. In contrast, the C-films obtained from deposition in 200 mTorr of N<sub>2</sub> without atomic nitrogen exhibited poor substrate adhesion and were very soft. Finally, the C-N films also exhibited good thermal stability. RBS analysis of the films after thermal treatments in flowing N<sub>2</sub> up to 800°C showed no observable loss of nitrogen. These characteristics (adhesion, hardness and thermal stability) were all suggestive of extended C-N covalent bonding in the films.

The structure of these new C-N materials was also investigated with electron diffraction. Transmission